The 4,4′-dimethoxytrityl carbenium ion by deamination of 4,4′-dimethoxytritylamine in acetonitrile–aqueous perchloric acid: kinetics, equilibria, deuterium isotope effects, and possible ion-pair formation

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The rate of deamination of 4,4′-dimethoxytritylammonium cation, generated from the corresponding amine in aqueous perchloric acid containing a low proportion of acetonitrile at constant total perchlorate concentration, is first order in both dimethoxytritylammonium and hydronium ions. The specificity of the hydronium ion kinetic effect indicates acid catalysis with second-order rate constant, k_H. There is also appreciable reactivity at $[H_3O^+] = 0$, *i.e.* an uncatalysed (solvent-induced) reaction channel from the substituted tritylammonium cation with first-order rate constant, k_o. The deuterium solvent kinetic isotope effects upon uncatalysed and catalysed reaction channels have been measured [$k_o^H/k_o^D = 1.51$ (±0.03), $k_H^H/k_H^D = 1.2$ (±0.1), 25 °C and ionic strength = 1 mol dm^{-3}]. The deuterium solvent isotope effect upon the subsequent equilibrium between 4,4′-dimethoxytrityl trityl cation and water (to give the substituted alcohol and hydronium ion) extrapolated to zero perchlorate concentration has also been determined, and the value $(K_{R^+})^H/(K_{R^+})^D = 3.4$ (±0.4) leads to a fractionation factor of *ca.* unity for the alcohol. The deamination is accelerated by increasing perchlorate concentrations at constant acidity; perchlorate also appears to have an appreciable effect upon the subsequent equilibrium involving the substituted trityl cation, water, hydronium ion, and the alcohol. Acetic acid, monochloroacetic acid, and trifluoroethanol also enhance the rate but not, apparently, by general acid catalysis, whereas the rate and final equilibrium are relatively insensitive to the proportion of the acetonitrile cosolvent. A mechanism for deamination is proposed which involves initial reversible heterolysis of the carbon–nitrogen bond of the tritylammonium cation followed by parallel diffusional separation and hydronium ion assisted separation. On the basis of the isotope effects, we conclude that the latter reaction channel involves either step-wise protonation of the ammonia molecule followed by rate-limiting separation of the cation–cation pair, or a strongly asynchronous (uncoupled) concerted process. Perchlorate may exert its appreciable kinetic and equilibrium effects simply by modifying the nature of the medium, *i.e.* by specific kinetic salt effects upon the various elementary steps in the overall reaction. Alternatively, the effect of perchlorate upon the final equilibrium may be explained by the reversible formation of specific ion-pairs between the extensively delocalised substituted trityl cation and the non-polarising perchlorate anion; we found no evidence of covalent dimethoxytrityl perchlorate. Correspondingly, the effect of perchlorate upon the observed *pseudo* first-order deamination rate constant could be due to its direct involvement in additional solvent-induced and hydronium ion-catalysed routes.

Introduction

Substituted tritylamines, Ar′Ar″Ar‴CNH$_2$, react in aqueous acidic solution to give equilibrium mixtures of the corresponding alcohols, Ar′Ar″Ar‴COH, the carbocations, Ar′Ar″Ar‴C$^+$, and NH$_4^+$, and the overall reaction is described by Scheme 1 where R = Ar′Ar″Ar‴C.

$$RNH_2 + H_3O^+ \rightleftharpoons RNH_3^+ + H_2O$$

$$RNH_3^+ \longrightarrow R^+ + NH_3$$

$$R^+ + 2H_2O \rightleftharpoons ROH + H_3O^+$$

$$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$$

Scheme 1

The *pseudo* first-order rate constant for the overall reaction and the composition of the final equilibrium depend upon the experimental conditions and the substituents in the aryl rings.[1,2] Although the unsubstituted parent compound Ph$_3$CNH$_2$ shows no appreciable reactivity in moderate concentrations of aqueous strong acids, electron-donating groups at the *para*-positions of the aryl rings increase the reactivity and promote the formation of the carbenium ions. Thus, for Ar′ = Ar″ = Ph and Ar‴ = 4-MeOC$_6$H$_4$ (monomethoxytritylamine, MMTNH$_2$), the reaction requires high acid concentrations to generate appreciable concentrations of the carbenium ion at equilibrium and is slow, but for Ar′ = Ar″ = Ar‴ = 4-MeOC$_6$H$_4$ (trimethoxytritylamine, TMTNH$_2$), the reaction is fast and gives a high yield of the carbenium ion at low acid concentrations. Between these two lies the amine with Ar′ = Ph and Ar″ = Ar‴ = 4-MeOC$_6$H$_4$ (dimethoxytritylamine, DMTNH$_2$), the subject of this investigation.

Previous studies by Bleasdale *et al.*[1] on the deamination of these tritylamines using methanolic aqueous acidic media showed that the reactions are subject to appreciable kinetic salt effects and, amongst cations, hydronium is particularly effective in accelerating the rate. If the hydronium ion rate-enhancing effect is specific acid catalysis, the alkylammonium cation plus an extra proton are involved in the rate-determining step of the acid-catalyzed reaction channel. Because there is no site for

$$RNH_3^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [R^+\cdot NH_3] \qquad (1)$$

$$[R^+\cdot NH_3] \xrightarrow{k_d} R^+ + NH_3 \qquad (2)$$

$$[R^+\cdot NH_3] + H_3O^+ \xrightarrow{k_a} R^+ + NH_4 + H_2O \qquad (3)$$

$$R^+ + 2H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ROH + H_3O^+ \qquad (4)$$

$$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$$

Scheme 2

direct initial protonation of the alkylammonium cation, the mechanism in Scheme 2 was tentatively proposed in the knowledge that, under the acidic conditions employed, the strongly basic tritylamines exist virtually entirely as the tritylammonium cations.[3,4] This mechanism involves reversible heterolysis of the tritylammonium cation to give the carbenium ion–ammonia (cation–molecule) pair, step (1), which then undergoes dissociation facilitated by protonation of the ammonia molecule, step (3). The uncatalysed reaction channel could involve diffusional separation of the cation–ammonia pair, step (2) in this mechanism, or simply unassisted unimolecular heterolysis of the original tritylammonium cation by-passing the ion–molecule pair (not shown in Scheme 2).

The primary aim of the present work was to probe in more detail the manner by which hydronium ion facilitates this deamination, *i.e.* to confirm (or prove otherwise) that the mechanism is specific acid catalysis as opposed to a specific kinetic salt effect (medium effect). Secondly, we aimed to characterise the uncatalysed reaction. A third aim was to quantify the influence of other solutes (especially perchlorate and general acids), and the composition of the solvent, upon the kinetics of this deamination. Finally, we intended to investigate the post-equilibrium between the substituted trityl cation and water, step (4) in Scheme 2. In the analysis of our data, we took account of results obtained in our concurrent study of the ionization of 4,4′-dimethoxytrityl alcohol (DMTOH) under the same acidic reaction conditions.[5]

Experimental

Materials

Glass distilled water and HPLC grade acetonitrile were used throughout, perchloric acid and hydrochloric acid were Fisons A.R. grade, and acid concentrations were determined by titration with standard aqueous sodium hydroxide. For the investigation of solvent isotope effects, solutions were made up using deuterium oxide (Aldrich, 100.0 atom% ^2H) and [^2H]perchloric acid (Aldrich, 68 wt.% solution in ^2H_2O; >99 atom% ^2H). 4,4′-Dimethoxytrityl alcohol and 4,4′-dimethoxytritylamine were available from previous work.[1,6] All other reagents were commercial products of A.R. grade.

Kinetics and equilibrium measurements

Reactions were initiated by the addition of the amine as a standard solution in pure acetonitrile using a Socorex micropipette to a measured volume of the aqueous or acetonitrile–aqueous acidic solution of known composition and concentration in a 1 cm path length quartz UV cell. Reactions were usually carried out at constant ionic strength (using sodium perchlorate when necessary) in the thermostatted cell block of a Cecil Instruments CE5502 double beam spectrophotometer interfaced to an Elonex PC433 microcomputer. Spectra of the reaction mixture recorded at different times (Fig. 1) show the development of an intense absorption band in the visible region due to the formation of the carbocation.

The kinetics of deamination of $DMTNH_2$ were studied by monitoring the increase with time of the absorbance at 495 nm, the wavelength of the maximum in the absorption spectrum of the carbocation. Except where indicated, the absorbance–time data were collected for at least four half-lives of the reaction, and were fitted to the integrated first-order rate equation where

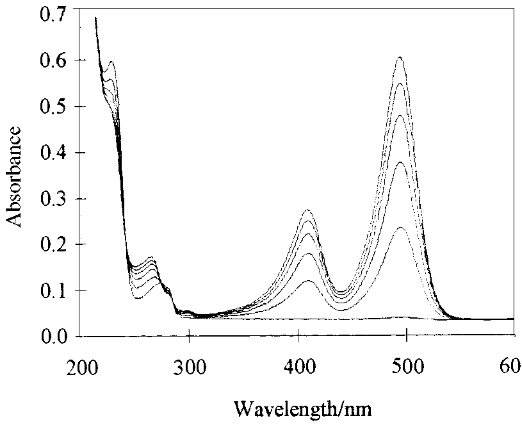

Fig. 1 Spectra of the reaction mixture at different times. $[HClO_4] = 1.0$ mol dm^{-3}, $[DMTNH_2]_0 = 2.58 \times 10^{-5}$ mol dm^{-3}, ionic strength = 1.0 mol dm^{-3} ($NaClO_4$), $T = 298$ K, 1% CH_3CN, $\Delta t = 2$ h.

$$A_t = A_0 + \Delta A(1 - \exp\{-k_{obs}t\})$$

A_0 is the absorbance at time $t = 0$, A_t is the absorbance at time t, and ΔA is the overall change in absorbance (from time = 0 to time = infinity) using a non-linear regression analysis program.[7] The errors on individual values of the rate constants k_{obs} were invariably less than 1% and, in repeated experiments, k_{obs} was reproducible to better than ±3%. Statistical treatment of errors was carried out using standard procedures.[8]

From step (4) in Scheme 2, we can derive the relationship in eqn. (5) between ΔA and the equilibrium constant K_{R^+}

$$\Delta A = \frac{[RNH_3^+]_0 \varepsilon_{R^+}}{\left(\dfrac{K_{R^+}}{[H_3O^+]} + 1\right)} \qquad (5)$$

($=k_2/k_{-2}$) where $[RNH_3^+]_0$ = initial concentration of the alkylammonium cation in the reaction mixture, and ε_{R^+} = molar absorptivity (extinction coefficient) of the carbocation. Using optimized values of ΔA from kinetics experiments at different acidities in a plot of $[RNH_3^+]_0/\Delta A$ against $[H_3O^+]^{-1}$, therefore, it is possible in principle to determine values of ε_{R^+} and K_{R^+}.[6]

Results

The effect of perchloric acid upon the observed *pseudo* first-order rate constant, k_{obs}, at 25 °C and constant total perchlorate concentration in 2% acetonitrile–water is shown in Table 1 together with the results obtained with deuterium oxide (^2H_2O, henceforth D_2O and L is used for ^1H or ^2H) in place of protium oxide. As expected from earlier studies in aqueous methanol,[1] there is a modest linear increase in the observed rate constant with increasing hydronium ion concentration at a constant total perchlorate concentration of 1.0 mol dm^{-3} (Fig. 2). The experimental first-order rate law may be expressed as eqn. (6)

$$k_{obs} = k_o + k_H[L_3O^+] \qquad (6)$$

where k_o is the first-order rate constant for the uncatalyzed (solvent-induced) process, and k_H is the second-order rate constant for the acid-catalyzed process. Values for both in H_2O and D_2O were obtained by linear regression and are given under Table 1.

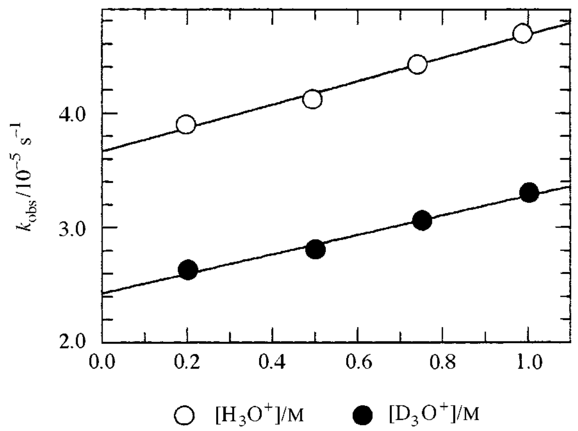

Fig. 2 Influence of acidity and solvent isotope effect upon the observed rate constant for deamination of $DMTNH_2$ in 2% CH_3CN–water, 298 K, ionic strength = 1 mol dm^{-3} ($NaClO_4$)

Table 1 Influence of acidity upon the deamination of $DMTNH_2$; 2% CH_3CN in H_2O and ^2H_2O, 25 °C, ionic strength = 1.0 mol dm^{-3} ($NaClO_4$)

$[H_3O^+]$/ mol dm^{-3}	$[D_3O^+]$/ mol dm^{-3}	$\Delta A/10^4$ $[DMTNH_2]_0$	$k_{obs}{}^a/10^{-5}$ s^{-1}	K_{R^+}
0.1975		0.63 ± 0.03	3.90 ± 0.05	2.0 ± 0.1
0.4938		1.45 ± 0.04	4.12 ± 0.02	1.89 ± 0.07
0.7408		2.07 ± 0.07	4.42 ± 0.05	1.76 ± 0.08
0.9877		2.60 ± 0.09	4.69 ± 0.05	1.67 ± 0.07
	0.202	1.72 ± 0.08	2.63 ± 0.09	0.62 ± 0.03
	0.501	3.3 ± 0.1	2.81 ± 0.05	0.56 ± 0.02
	0.752	4.1 ± 0.1	3.06 ± 0.06	0.53 ± 0.02
	1.003	4.6 ± 0.1	3.3 ± 0.1	0.52 ± 0.02

[a] Observed rate constants are average values from three kinetic runs. Linear regression of the results in H_2O gives $k_o{}^H = 3.67\ (\pm 0.05) \times 10^{-5}$ s^{-1} and $k_H{}^H = 1.02\ (\pm 0.07) \times 10^{-5}$ dm^3 mol^{-1} s^{-1} ($R = 0.995$); corresponding values in D_2O are $k_o{}^D = 2.43\ (\pm 0.04) \times 10^{-5}$ s^{-1} and $k_H{}^D = 0.86\ (\pm 0.09) \times 10^{-5}$ dm^3 mol^{-1} s^{-1} ($R = 0.994$).

From these experiments and eqn. (5), it is also possible to determine ε_{R^+} and K_{R^+}.[6] However, this involves a large extrapolation for ε_{R^+} which leads to an appreciable uncertainty. Consequently, we determined ε_{R^+} from UV absorption measurements of standard solutions of the carbocation generated from the alcohol and chloride in concentrated perchloric and hydrochloric acids.[5] A consistent value of $\varepsilon_{R^+} = 7.0\ (\pm 0.2) \times 10^4$ dm^3 mol^{-1} cm^{-1} was obtained from which values of K_{R^+} were then determined using eqn. (5) and are included in Table 1; the average values are $K_{R^+} = 1.8\ (\pm 0.1)$ in H_2O and 0.56 (±0.04) in D_2O at 1.0 mol dm^{-3} total perchlorate concentration. The result $\varepsilon_{R^+} = 7.0\ (\pm 0.2) \times 10^4$ dm^3 mol^{-1} cm^{-1} is appreciably smaller than an earlier value of 30×10^4 dm^3 mol^{-1} cm^{-1}.[6,9] However, the present result is more in line with earlier values of between 60 350 and 104 700 dm^3 mol^{-1} cm^{-1} for the trimethoxytrityl cation.[10,11]

In Table 2, we see that replacing sodium perchlorate by ammonium perchlorate has no significant kinetic effect at constant acidity and constant total perchlorate concentration; the same had been found earlier for replacing sodium perchlorate by lithium perchlorate in aqueous acidic methanol.[1] Effects of acetic acid, monochloroacetic acid, and trifluoroethanol were also investigated at constant H_3O^+ concentration, and the results are included in Table 3; all lead to modest linear increases in k_{obs}. The effect upon the observed rate constant of changing the total perchlorate concentration at constant acidity was studied in protio- and deuterio-solvents, but not at constant ionic strength. Results are summarized in Table 4 and, for the protio-solvent, Fig. 3 shows the linear increase in the observed rate constant with the increasing total perchlorate concentration.

Table 2 Effect of replacing sodium by ammonium ions upon the observed rate constant for deamination of $DMTNH_2{}^a$; $[HClO_4] = 0.195$ mol dm^{-3}, ionic strength = 1.0 mol dm^{-3} (perchlorate), 2% CH_3CN in water, 25 °C

$[NH_4{}^+]$/mol dm^{-3}	$[Na^+]$/mol dm^{-3}	ΔA	$k_{obs}/10^{-5}$ s^{-1}
0.1985	0.8015	0.315	3.70
0.3969	0.6031	0.270	3.61
0.5954	0.4046	0.290	3.56
0.7939	0.2061	0.260	3.54

[a] $[DMTNH_2]_0 = 5.32 \times 10^{-5}$ mol dm^{-3}.

We also determined the apparent equilibrium constant K_{R^+} in H_2O for different total perchlorate concentrations from the values of ΔA in Table 4 using eqn. (5) and, by extrapolation, estimated its value at zero perchlorate concentration. The result, $K_{R^+} = 12 \pm 1$ ($pK_{R^+} = -1.08$), is in good agreement with our result starting from the alcohol[5] and with literature values.[9,12–14] In the same way, we determined the apparent K_{R^+} in D_2O for different total perchlorate concentrations, and the estimated value at zero perchlorate concentration is 3.5 ± 0.3 (as in the determination in H_2O, an error of *ca.* 10% is assumed in the non-linear extrapolation). The deuterium solvent isotope effect upon the equilibrium constant at zero perchlorate concentration, therefore, is $(K_{R^+})^H/(K_{R^+})^D = 3.4 \pm 0.4$. This equilibrium solvent isotope effect compares with a value of 2.7 determined for the trimethoxytrityl system,[15] and leads to a fractionation factor for dimethoxytrityl alcohol of 0.9 ± 0.1, *i.e.* virtually unity, the expected value for alcohols in general[16] and in good agreement with values reported for trityl alcohols in particular.[10,17]

Although replacement of sodium by ammonium (or lithium)[1] has no significant effect on the observed rate constant, replacement of perchlorate by chloride at constant acidity appreciably decreases the rate constant, Table 5. In these reactions, however, a fine precipitate formed (believed to be dimethoxytrityl alcohol)[11] which limited the collection of reliable data to about the first 60% of the reaction. Very similar results were obtained when sodium perchlorate was replaced by sulfamic acid, Table 6, but again, the fine precipitate formed and we were able to monitor these reactions for only about two half-lives. Both sets of results were obtained at constant ionic strength and are included in Fig. 3.

A comparison of the effects of perchloric and hydrochloric acids upon the observed rate constant was also made but under conditions of non-constant ionic strength, and the results are summarized in Table 7. In the case of hydrochloric acid, the fine precipitate believed to be dimethoxytrityl alcohol again formed,[11] which limited the collection of reliable data to about the first 60% of the reaction. Up to about 1 mol dm^{-3}, there is a modest approximately linear effect of hydrochloric acid concentration upon k_{obs}. The effect is much larger for perchloric acid, but with marked upwards curvature even at these fairly low concentrations; in fact, the correlation of k_{obs} with $[HClO_4]^2$ is linear ($R = 0.997$).

Table 8 illustrates the very modest effect upon rate and equilibrium constants of increasing the percentage of acetonitrile in the aqueous medium from 1 to 60% at constant acidity. A similarly small equilibrium effect has been reported earlier for the parent trityl system.[18] Table 9 shows the effect of increasing the acidity (at constant total perchlorate concentration) at 20% acetonitrile–water for comparison with results at 2%; clearly, the effects are very similar.

Discussion

Hydronium ion catalysis *via* ion–molecule pairs

Whereas replacement of sodium cation by ammonium, or by lithium in aqueous methanol,[1] has no appreciable kinetic effect,

Table 3 Influence of $ClCH_2COOH$, CH_3COOH, and CF_3CH_2OH upon the deamination of $DMTNH_2$[a] in 2% CH_3CN–water; 25 °C, $[HClO_4] = 0.1975$ mol dm^{-3}, ionic strength = 1.0 mol dm^{-3} ($NaClO_4$)

$[ClCH_2CO_2H]$ /mol dm^{-3}	$[CH_3CO_2H]$ /mol dm^{-3}	$[CF_3CH_2OH]$ /mol dm^{-3}	ΔA	$k_{obs}/10^{-5}$ s^{-1}	K_{R^+}
0.10			0.32 ± 0.05	3.8[b] ± 0.3	2.10
0.40			0.436 ± 0.002	4.68[b] ± 0.02	1.49
0.70			0.508 ± 0.005	5.44[b] ± 0.02	1.25
1.00			0.606 ± 0.006	6.34[b] ± 0.07	1.02
	0.100		0.341	3.81	1.96
	0.401		0.375	4.02	1.76
	0.702		0.416	4.34	1.57
	1.003		0.456	4.62	1.42
		0.103	0.352	4.00	1.89
		0.403	0.377	4.30	1.75
		0.703	0.442	4.72	1.47
		1.002	0.507	5.18	1.25

[a] $[DMTNH_2]_0 = 5.32 \times 10^{-5}$ mol dm^{-3}. [b] Averaged values of two kinetic runs.

Table 4 Effect of total perchlorate[a] concentration upon the deamination of $DMTNH_2$; $[L_3O^+] = 0.20$ mol dm^{-3} (L = H or ^2H), 25 °C, 2% CH_3CN in water, ionic strength not constant

Solvent	$[DMTNH_2]_0$/mol dm^{-3}	$[ClO_4^-]_{Total}$/mol dm^{-3}	ΔA	$k_{obs}/10^{-5}$ s^{-1}	K_{R^+}
H_2O	5.16×10^{-5}	0.20	0.089	1.93	7.82
		0.40	0.134	2.39	5.13
		0.70	0.210	3.05	3.20
		1.00	0.321	3.91	2.02
^2H_2O	2.66×10^{-5}	0.20	0.148	1.29	2.30
		0.40	0.222	1.53	1.47
		0.70	0.334	2.04	0.91
		1.00	0.471	2.53	0.59

[a] Total perchlorate = perchloric acid plus sodium perchlorate.

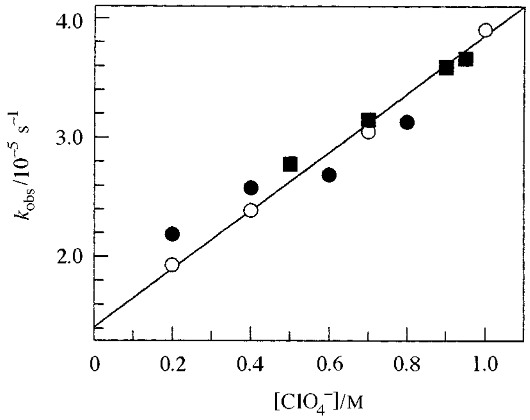

Fig. 3 Influence of total perchlorate concentration on the observed rate constant. $[DMTNH_2]_0 = 5.16 \times 10^{-5}$ mol dm^{-3}, $[HClO_4] = 0.20$ mol dm^{-3}, 2% CH_3CN in water, 25 °C. ○ are for the influence of ClO_4^- in the absence of other anions, ● are for ClO_4^- in the presence of Cl^-, and ■ are for ClO_4^- in the presence of sulfamic acid (ionic strength = 1.0 mol dm^{-3} in the last two experiments).

its replacement by hydronium at constant ionic strength leads to a distinct linear increase in the observed first-order rate constant. From the specificity of this effect, we conclude that hydronium ion is indeed a genuine catalyst. The experimental results in Table 1 are described by the rate law of eqn. (6) above, and linear regression of k_{obs} against $[L_3O^+]$ for water and deuterium oxide yields k_o^L and k_H^L. The four values are given below Table 1 and from them we calculate $k_o^H/k_o^D = 1.51$ (±0.03) and $k_H^H/k_H^D = 1.2$ (±0.1) at 25 °C and ionic strength = 1 mol dm^{-3}. The former is difficult to reconcile with an uncatalysed reaction involving simple rate-determining unimolecular heterolysis of the tritylammonium cation; such a mechanism with residual bonding between the carbon and nitrogen in the transition structure should lead to a deuterium solvent kinetic isotope effect much closer to unity. And the latter value seems low for a catalytic mechanism involving rate-limiting proton transfer.

Table 5 Effect of replacing sodium perchlorate by sodium chloride upon the observed rate constant for deamination of $DMTNH_2$[a]; $[H_3O^+] = 0.1975$ mol dm^{-3}, ionic strength = 1.0 mol dm^{-3}, 2% CH_3CN in water, 25 °C

[NaCl]/ mol dm^{-3}	$[\text{Perchlorate}]_{Total}$[b]/ mol dm^{-3}	ΔA[c]	k_{obs}[c]$/10^{-5}$ s^{-1}
0.20	0.80	0.284 ± 0.004	3.13 ± 0.08
0.40	0.60	0.231 ± 0.004	2.69 ± 0.04
0.60	0.40	0.189 ± 0.005	2.58 ± 0.03
0.80	0.20	0.150 ± 0.003	2.19 ± 0.05

[a] $[DMTNH_2]_0 = 5.32 \times 10^{-5}$ mol dm^{-3}. [b] Total perchlorate = perchloric acid plus sodium perchlorate. [c] These reactions were monitored for only 1.5 half lives; ΔA and k_{obs} values are the average results from duplicate kinetic runs.

Table 6 Effect of replacing sodium perchlorate by sulfamic acid upon the observed rate constant for deamination of $DMTNH_2$[a]; $[HClO_4] = 0.1974$ mol dm^{-3}, ionic strength = 1.0 mol dm^{-3} ($NaClO_4$), 2% CH_3CN in water, 25 °C

$[H_3NSO_3]$/ mol dm^{-3}	$[\text{Perchlorate}]_{Total}$[b]/ mol dm^{-3}	ΔA	$k_{obs}/10^{-5}$ s^{-1}
0.05	0.95	0.336	3.66
0.10	0.90	0.328	3.59
0.30	0.70	0.294	3.15
0.50	0.50	0.252	2.78

[a] $[DMTNH_2]_0 = 5.32 \times 10^{-5}$ mol dm^{-3}; reactions were monitored for about two half-lives. [b] Total perchlorate = perchloric acid plus sodium perchlorate.

Scheme 2 had been proposed to provide mechanisms for catalysed and uncatalysed reaction channels *via* an ion–molecule pair intermediate. By applying the steady-state approximation to this intermediate, the following equation for the observed first-order rate law may be derived assuming $k_{-1} \gg k_d + k_a[H_3O^+]$:[1,2] where $K_1 = k_1/k_{-1}$. By comparing eqn. (7) with

$$k_{obs} = K_1k_d + K_1k_a[H_3O^+] \quad (7)$$

Table 7 Influence of perchloric and hydrochloric acids upon the observed rate constant of deamination of $DMTNH_2$[a]; 2% CH_3CN in water, 25 °C, ionic strength not constant

$[HClO_4]$/mol dm^{-3}	$[HCl]$/mol dm^{-3}	ΔA	$k_{obs}/10^{-5}$ s^{-1}
0.1975		0.098	1.88
0.4938		0.451	2.71
0.7408		0.923	3.50
0.9877		1.516	4.70
	0.20	0.082	0.98
	0.50	0.231	1.52
	0.75	0.433	1.77
	1.00	0.712	1.95

[a] $[DMTNH_2]_0 = 5.32 \times 10^{-5}$ mol dm^{-3}; reactions were monitored only for 1.5 half lives in the hydrochloric acid (see text).

Table 8 Influence of the solvent composition upon the deamination of $DMTNH_2$[a] in aqueous acetonitrile; $[HClO_4] = 0.9877$ mol dm^{-3}, 25 °C

% CH_3CN in water	ΔA	k_{obs}[b]$/10^{-5}$ s^{-1}	K_{R^+}
1	0.640 ± 0.020	4.59 ± 0.03	2.09
20	0.590 ± 0.010	5.34 ± 0.03	2.35
40	0.474 ± 0.007	5.27 ± 0.06	3.17
60	0.620 ± 0.030	6.48 ± 0.07	2.19

[a] $[DMTNH_2]_0 = 2.85 \times 10^{-5}$ mol dm^{-3}. [b] Rate constants are average results from two experiments.

Table 9 Effect of acid concentration upon the deamination of $DMTNH_2$[a] in 20% CH_3CN–water, ionic strength = 1.0 mol dm^{-3} ($NaClO_4$), 25 °C

$[HClO_4]$/mol dm^{-3}	ΔA	$k_{obs}/10^{-5}$ s^{-1}	K_{R^+}
0.1975	0.279	4.26	2.36
0.4938	0.686	4.67	2.11
0.7408	1.005	5.05	1.92
0.9877	1.279	5.39	1.80

[a] $[DMTNH_2]_0 = 5.16 \times 10^{-5}$ mol dm^{-3}.

eqn. (6), we see that $k_o = K_1k_d$ and $k_H = K_1k_a$; consequently, $(K_1k_d)^H/(K_1k_d)^D = 1.51 \pm 0.03$ and $(K_1k_a)^H/(K_1k_a)^D = 1.2 \pm 0.1$. By assuming that the solvent deuterium kinetic isotope effect for a diffusion-controlled reaction is given by the ratio of the viscosities of deuterium oxide and water,[19] *i.e.*, $k_d^H/k_d^D = \eta_{D_2O}/\eta_{H_2O} = 1.24$, we obtain $K_1^H/K_1^D = 1.22$ and, consequently, $k_a^H/k_a^D = 0.98$ (~1.0). The former secondary deuterium isotope effect of 1.22 for the heterolytic pre-equilibrium of step (1) compares well with the result of 1.17 calculated from literature values for the fractionation factors for N–H and N$^+$–H.[16] This supports the proposal that the uncatalysed reaction is *via* rate-limiting diffusion apart from the ion–molecule pair and not by simple direct heterolysis of the original tritylammonium cation.

However, if step (3) in Scheme 2 involves hydron transfer between two hetero atoms coupled with the heavy atom reorganisation, *i.e.* a fully synchronous concerted process, and is rate-limiting in the catalysed reaction, then a deuterium kinetic isotope effect appreciably greater than unity would be observed.[20] The experimental result of $k_a^H/k_a^D = $ ~1.0, therefore, is not credible and indicates that the proposed mechanism in Scheme 2 requires revision.

Further evidence that proton transfer is not a significant feature of the rate-determining step in the catalysed reaction comes from the effect of different weak acids upon the observed rate constant, Table 3. The gradients of the linear plots of k_{obs} against the concentrations of acetic acid, chloroacetic acid, and trifluoroethanol at constant hydronium ion concentration are 0.92 (±0.05) × 10^{-5} ($R = 0.996$), 2.79 (±0.06) × 10^{-5} ($R = 0.999$), and 1.32 (±0.09) × 10^{-5} dm^3 mol^{-1} s^{-1} ($R = 0.996$). Whilst the effect of chloroacetic acid is larger than that of acetic acid, the effect of trifluoroethanol is also larger than that of acetic acid; moreover, both chloroacetic acid and trifluoroethanol appear more effective than H_3O^+. These results are not compatible with a rate-limiting proton transfer mechanism involving these solutes acting as catalytic general acids in view of their relative acid strengths.[3,4] We conclude that the increasing observed rate constants due to increasing concentrations of monochloroacetic acid, acetic acid, and trifluoroethanol are medium effects.

$$RNH_3^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [R^+\cdot NH_3] \qquad (1)$$

$$[R^+\cdot NH_3] \xrightarrow{k_d} R^+ + NH_3 \qquad (2)$$

$$[R^+\cdot NH_3] + H_3O^+ \underset{k_{-1'}}{\overset{k_{1'}}{\rightleftharpoons}} [R^+\cdot NH_4^+] + H_2O \qquad (3a)$$

$$[R^+\cdot NH_4^+] \xrightarrow{k_{d'}} R^+ + NH_4^+ \qquad (3b)$$

$$R^+ + 2H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ROH + H_3O^+ \qquad (4)$$

$$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$$

Scheme 3

On the basis of these results, we proposed first that step (3) in Scheme 2 be resolved into a reversible protonation to give an ammonium–carbocation pair, step (3a) in Scheme 3, followed by rate-limiting diffusional separation of this cation–cation pair, step (3b), *i.e.* the synchronous concerted reaction be replaced by a stepwise alternative.

According to this revised mechanism and the usual assumptions, the rate law is now given by eqn. (8) (where $K_{1'} = k_{1'}/k_{-1'}$

$$k_{obs} = K_1k_d + K_1K_{1'}k_{d'}[H_3O^+] \qquad (8)$$

in Scheme 3) and, by comparing this with eqn. (6), we obtain $k_o = K_1k_d$ for the uncatalyzed term as before. But now, $k_H = K_1K_{1'}k_{d'}$ for the catalyzed reaction channel. As determined above, $K_1^H/K_1^D = 1.22$ and, as before, we assume a solvent deuterium kinetic isotope effect for the second diffusion controlled reaction, $k_{d'}^H/k_{d'}^D = 1.24$; thus, we now calculate $K_{1'}^H/K_{1'}^D = 0.79$. This result of less than unity for the equilibrium hydron transfer between hetero atoms is qualitatively as expected since D_3O^+ is a stronger acid than H_3O^+;[20] however, a simple calculation using fractionation factor theory[16] leads to a result of 0.3. In other words, the experimental solvent deuterium kinetic isotope effect result for the acid-catalysed reaction appears too large on the basis of (admittedly) simple calculations for the stepwise mechanism of Scheme 3, but too small on the basis of the synchronous concerted mechanism in Scheme 2.

It is important to appreciate the difference between the mechanisms of Schemes 2 and 3. In the latter, a separate reversible proton transfer, step (3a), precedes the rate-limiting heavy atom reorganisation, the cation–cation pair is a discrete intermediate, and the transition structure involves no vestigial bond between the nitrogen and the central carbon of the carbenium ion. In Scheme 2, the proton transfer and heavy atom reorganisation are concerted and, by implication, synchronous, so the transition structure includes partial bonding between nitrogen and carbon. However, the proton transfer and heavy atom reorganisation could be forced to be concerted by an intermediate (the cation–cation pair) which is too unstable to exist. In this case, the present results require that the two principal components of the concerted reaction (hydron transfer and dissociation) are strongly asynchronous (uncoupled), *i.e.* the transition structure includes very little bonding between the nitrogen of the nucleofuge and the incipient carbenium ion. Such a mechanism would accommodate the absence of kinetic general acid catalysis. Our computational methods are insufficiently refined to allow us to estimate the solvent isotope effect for such a mechanism, but it should lie between the limits set by the fully synchronous concerted mechanism and the fully stepwise extremes and be in accord with our experimental value.

The effect of perchlorate upon k_{obs} and K_{R^+}

(i) Kinetic salt effect model. Our results in Table 4 show the relationship between the observed rate constant and total perchlorate concentration. By linear regression ($R = 0.998$), we obtain a value of 1.41 (±0.07) × 10^{-5} s^{-1} for the intercept (k_{obs} when $[ClO_4^-] = 0$), and 2.4 (±0.1) × 10^{-5} dm^3 mol^{-1} s^{-1} for the gradient. The latter result represents the sensitivity of the observed rate constant to the total perchlorate concentration at constant $[H_3O^+]$, and is more than twice as large as the sensitivity of k_{obs} to the concentration of hydronium ions, *i.e.* $k_H^{\,H}$, at constant $[ClO_4^-]$. The plot of k_{obs} *versus* the total concentration of ClO_4^- in D_2O is also a straight line ($R = 0.998$) with intercept = 0.94 (±0.04) × 10^{-5} s^{-1} and slope = 1.57 (± 0.06) × 10^{-5} dm^3 mol^{-1} s^{-1}, the latter value being almost twice the size of $k_H^{\,D}$, *i.e.*, the effect of D_3O^+ upon k_{obs}. In Tables 5 and 6, we see the effect of replacing sodium perchlorate by sodium chloride and by sulfamic acid, $^+NH_3SO_3^-$. The observed rate constant is reduced as perchlorate is replaced at constant total ionic strength and constant acidity, and we conclude, in accord with earlier researchers,[21,22] that perchlorate is particularly effective in promoting the formation of large delocalised carbenium ions. One explanation of these results is that they are due to specific salt effects upon the elementary rate constants brought about by changes in the nature of the medium. This explanation is consistent with the effects of the three protic cosolvents upon observed rate constants (Table 3), but seemingly not with the minimal effect of the composition of the aqueous acetonitrile (Tables 8 and 9).

(ii) Effect of perchlorate upon the final equilibrium. We observe in Table 4 the effect of total perchlorate upon the apparent equilibrium constant K_{R^+} defined in eqn. (4) of Schemes 2 and 3 for the reaction of the carbenium ion with water: $K_{R^+} = 12 \pm 1$ in H_2O and 3.5 ± 0.3 in D_2O at zero perchlorate concentration compared with values of 1.8 (±0.1) in H_2O and 0.56 (±0.04) in D_2O at 1.0 mol dm^{-3} total perchlorate concentration. Thus, although the absolute values are very different according to the presence or otherwise of 1.0 mol dm^{-3} total perchlorate concentration, the solvent isotope effect (within experimental error) is not. The mechanism for the k_{-2} direction in eqn. (4) will involve protonation of the hydroxy followed by departure of water as nucleofuge, *i.e.* like the mechanism proposed for the deamination, the rate of which is enhanced by increasing concentrations of perchlorate. Consequently, we may anticipate an analogous (rate-enhancing) effect by perchlorate upon k_{-2}. The overall effect of perchlorate upon K_{R^+} is inverse (and actually numerically larger than its effect upon k_{obs}). The effect of perchlorate upon k_2 in step (4) of Scheme 2, therefore, must be appreciably smaller than its effect upon k_{-2}, and may even be of opposite sign, *i.e.* rate-retarding. In other words, according to this analysis, increasing concentrations of perchlorate increase k_{-2} but may actually decrease k_2; this is in accord with what was reported previously by Wyatt[21,22] for the 4,4′,4″-trimethoxytrityl alcohol system.

(iii) Possible equilibrium formation of dimethoxytrityl perchlorate ion-pairs. We found no spectroscopic evidence (UV–VIS, IR, and ^{13}C and ^{35}Cl NMR) for covalent dimethoxytrityl perchlorate,[23] and the parent trityl perchlorate is ionic in the crystalline state.[24] Consequently, we do not regard covalent dimethoxytrityl perchlorate as a credible molecule under our reaction conditions. However, equilibrium formation of dimethoxytrityl perchlorate ion-pairs is less easily dismissed, and they were invoked by Wyatt to reconcile H_R results obtained in sulfuric and perchloric acids.[22] In the present system, neglect of such ion-pairs (if they exist) would certainly account for the apparent effect of perchlorate upon K_{R^+} defined in eqn. (4) of Schemes 2 and 3 ($K_{R^+} = k_2/k_{-2}$). If ion-pairs do form, therefore, the following equilibrium has to be taken into account in Scheme 3.

$$R^+ + ClO_4^- \rightleftharpoons R^+\|ClO_4^-;\; K_{IP} = \frac{[R^+\|ClO_4^-]}{[R^+][ClO_4^-]}$$

If this equilibrium is incorporated, and we assume that the molar absorptivity of the ion-pairs is the same as that of the dissociated substituted trityl cations, then eqn. (5) has to be replaced by eqn. (9) which, in principle, allows determination of K_{IP} as well as K_{R^+}.

$$\Delta A = \frac{[R\overset{+}{N}H_3]_0\varepsilon_{R^+}(1 + K_{IP}[ClO_4^-])}{\left\{1 + \dfrac{K_{R^+}}{[H_3O^+]} + K_{IP}[ClO_4^-]\right\}} \qquad (9)$$

From the data in Table 5 (and assuming that inorganic chloride acts simply as an inert electrolyte), results of $K_{R^+} = 7.3$ (±0.5) and $K_{IP} = 2.5$ (±0.2) dm^3 mol^{-1} are obtained by linear regression ($R = 0.997$) of $\Delta A/(\varepsilon_{R^+}[RNH_3^+]_0 - \Delta A)$ against $[ClO_4^-]$ using a value of 7.0 × 10^4 dm^3 mol^{-1} cm^{-1} for ε_{R^+}. In view of the experimental difficulties using chloride as a solute (reactions could be monitored to only about 60% completion due to the formation of a precipitate, see above), this value for K_{R^+} is reasonable, and the value for K_{IP} is gratifyingly close to Wyatt's value[22] of 1.3 dm^3 mol^{-1} though this is probably fortuitous, and much smaller than the value for trityl perchlorate in the much less polar 1,2-dichloroethane (795 dm^3 mol^{-1}).[24]

(iv) Catalysis by perchlorate in the deamination reaction. As an alternative to a specific kinetic salt effect, *i.e.* a medium effect model, see (i) above, perchlorate could be directly involved in the reactions. This would correspond to the inclusion of extra terms in Scheme 3 to describe (a) perchlorate-assisted reaction of the ion–molecule pair, *i.e.* an additional uncatalysed route:

$$ClO_4^- + [R^+{\cdot}NH_3] \xrightarrow{k_{(ClO_4^-)}} ClO_4^-\|R^+ + NH_3$$

and (b) perchlorate-assisted reaction of the cation–cation pair, *i.e.* an additional acid-catalysed route:

$$ClO_4^- + [R^+{\cdot}NH_4^+] \xrightarrow{k'_{(ClO_4^-)}} ClO_4^-\|R^+ + NH_4^+$$

Incorporation of these two extra reaction channels into the kinetic analysis leads to eqn. (10), in place of eqn. (8), the fourth

$$k_{obs} = K_1k_d + K_1k_{(ClO_4^-)}[ClO_4^-] + K_1K_{1'}k_{d'}[H_3O^+] + K_1K_{1'}k'_{(ClO_4^-)}[ClO_4^-][H_3O^+] \qquad (10)$$

term of which accounts qualitatively for the observed squared dependence of k_{obs} upon the concentration of perchloric acid at non-constant ionic strength (Table 7, see above).

A non-linear regression analysis using twelve values of k_{obs} at various combinations of $[H_3O^+]$ and $[ClO_4^-]$ from Tables 1, 4, and 7 yields the following results in H_2O:[25]

$$K_1k_d = 1.37\ (\pm 0.05) \times 10^{-5}\ s^{-1}$$

$$K_1k_{(ClO_4^-)} = 2.28\ (\pm 0.08) \times 10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$$

$$K_1K_{1'}k'_{(ClO_4^-)} = 1.03\ (\pm 0.07) \times 10^{-6}\ dm^6\ mol^{-2}\ s^{-1}.$$

For the reaction in D_2O, the corresponding results are:

$$K_1k_d = 0.92\ (\pm 0.05) \times 10^{-5}\ s^{-1}$$

$$K_1k_{(ClO_4^-)} = 1.46\ (\pm 0.07) \times 10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$$

$$K_1K_{1'}k'_{(ClO_4^-)} = 0.91\ (\pm 0.06) \times 10^{-5}\ dm^6\ mol^{-2}\ s^{-1}.$$

Assuming again a solvent isotope effect of 1.2 for the diffusion controlled reactions,[19] then $k_d{}^H/k_d{}^D = 1.2$. Thus, the solvent isotope effect for the other elementary steps are:

$$(K_1)^H/(K_1)^D = 1.2 \pm 0.1 \qquad (k_{(ClO_4^-)})^H/(k_{(ClO_4^-)})^D = 1.3 \pm 0.1$$

$$(k'_{(ClO_4^-)})^H/(k'_{(ClO_4^-)})^D = 1.2 \pm 0.1 \qquad (K_{1'})^H/(K_{1'})^D = 0.8 \pm 0.1.$$

The bimolecular reactions involving the perchlorate ion, therefore, have solvent kinetic isotope effects the same as the ratio of the solvents' viscosities (*i.e.* like diffusion controlled reactions, which seems reasonable), and the hydron-transfer equilibrium has a solvent isotope effect lower than unity, exactly as expected since D_3O^+ is a stronger acid than H_3O^+.[20]

We conclude that an overall mechanism which includes involvement by perchlorate in the deamination and the formation of dimethoxytrityl perchlorate ion-pairs accounts at least as satisfactorily for the effect of perchlorate upon rate and equilibrium measurements as the alternative which ascribes the effect of perchlorate to specific kinetic salt (medium) effects. This being the case, perchlorate salts as electrolytes to maintain constant ionic strength may have been an unfortunate frequent choice in the past for reactions which involve relatively stable carbenium ion intermediates.

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References

1 C. Bleasdale, B. T. Golding, W. H. Lee, H. Maskill, J. Riseborough and E. Smits, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 93.

2 M. C. Lopez, J. Crugeiras, I. Demirtas, H. Maskill and E. Stix, *Org. React.*, 1997, **31**, 71.

3 A. Albert and E. P. Serjeant, in *The Determination of Ionisation Constants*, Chapman and Hall, London, 1984.

4 H. Maskill, in *The Physical Basis of Organic Chemistry*, Oxford University Press, Oxford, 1985.

5 J. Crugeiras and H. Maskill, unpublished results.

6 W. H. Lee and H. Maskill, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 1463.

7 R. J. Leatherbarrow, GraFit Version 3.0, Erithacus Software, Staines, 1992.

8 A. Finlay, in *Practical Physical Chemistry*, ed. by J. A. Kitchener, Longman, London, 8th edn., 1960.

9 N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.*, 1955, **77**, 3044.

10 V. Gold and C. Tomlinson, *J. Chem. Soc.* (*B*), 1971, 1707.

11 M. J. Postle and P. A. H. Wyatt, *J. Chem. Soc.*, *Perkin Trans. 2*, 1972, 474.

12 R. A. Cox and K. Yates, *Can. J. Chem.*, 1984, **62**, 2155.

13 M. J. Cook, N. L. Dassanayake, C. D. Johnson, A. R. Katritzky and T. W. Toone, *J. Am. Chem. Soc.*, 1975, **97**, 760.

14 E. M. Arnett and R. D. Bushick, *J. Am. Chem. Soc.*, 1964, **86**, 1564.

15 E. A. Hill and W. J. Mueller, *Tetrahedron Lett.*, 1968, 2565.

16 R. L. Schowen, *Prog. Phys. Org. Chem.*, 1972, **9**, 275.

17 M. M. Kreevoy and T. M. Liang, *J. Am. Chem. Soc.*, 1980, **102**, 3315.

18 N. Mathivanan, R. A. McClelland and S. Steenken, *J. Am. Chem. Soc.*, 1990, **112**, 8454.

19 B. H. Robinson, in *Proton-Transfer Reactions*, ed. E. F. Caldin and V. Gold, Chapman and Hall, London, 1975, p.133.

20 R. P. Bell, in *The Proton in Chemistry*, Chapman and Hall, London, 2nd edn., 1973.

21 H. Nicholson and P. A. H. Wyatt, *J. Chem. Soc.* (*B*), 1968, 198.

22 P. A. H. Wyatt, *J. Chem. Res.* (*S*), 1980, 297 and references cited therein.

23 N. S. Zefirov, A. S. Koz'min, V. V. Zhdankin, V. N. Kirin, N. M. Yur'eva and V. D. Sorokin, *Chem. Scr.*, 1983, **22**, 195; N. S. Zefirov and A. S. Koz'min, *Acc. Chem. Res.*, 1985, **18**, 154.

24 W. R. Longworth and C. P. Magon, *J. Chem. Soc.* (*A*), 1966, 1164.

25 There are terms in eqn. (10) corresponding to four reaction channels of RNH_3^+: (i) involving neither H_3O^+ nor ClO_4^+, (ii) involving ClO_4^-, (iii) involving H_3O^+, and (iv) involving both H_3O^+ and ClO_4^-. Regression analysis to evaluate the four combinations of parameters in eqn. (10) leads to a negative result for $K_1K_{1'}k_{d'}$ in the third term with a large (50%) error which makes no sense and is omitted. An estimate of this third term $K_1K_{1'}k_{d'} = 0.71$ $(\pm 0.07) \times 10^{-5}$ dm^3 mol^{-1} s^{-1} may be obtained from the reactions in hydrochloric acid, *i.e.* in the absence of perchlorate, if we assume that chloride anion itself does not provide a reaction channel. In support of this assumption, the data of Table 5 show that replacing ClO_4^- by Cl^- at constant ionic strength reduces k_{obs}, and the extrapolated value for k_{obs} at $[Cl^-] = 1$ mol dm^{-3} and $[H_3O^+] = 0.2$ mol dm^{-3} $(1.9 \times 10^{-5}\ s^{-1})$ is in good agreement with that extrapolated from the data in Table 4 for $[ClO_4^-] = 0$ at $[H_3O^+] = 0.2$ mol dm^{-3} $(1.4 \times 10^{-5}\ s^{-1})$.

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